COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1937

VOLUME XVI

№ 8

EDITION DE L'ACADÉMIE DES SCIENCES DE L'URSS
MOSCOU

Pages

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En composition: 17/VIII 1937.—En impression: 28/IX 1937.—Nombre de feuilles d'impression 3. Nombre de caractères par feuille d'impression 65.000.—Pages 385—432. Format du papier 72×110 cm. Tirage 1.200. Moscou. Glavlit B—15360.—Numéro d'édition 752. Numéro typographique 1258.

Imprimerie, № 16. Moscou, Trekhproudnij péréoulok, 9.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

MECHANICS

DETERMINATION OF INSTANTANEOUS STRESSES IN SKELETONS OF SOILS

By V. A. FLORIN

(Communicated by B. G. Galerkin, Member of the Academy, 22. VII. 1937)

The problem of the determination of stresses which occur in the skeleton of a soil (having all pores entirely filled by ground water) immediately after the application of a load at the surface of the ground,—has been solved by N. M. Guersevanov * for two cases of loading.

In both cases the problem is treated in two dimensions; in one case, the loading is represented by a strip uniformly loaded; in the other case, the diagram of loading begins at the origin of coordinates and extends in one direction to an infinite length.

This paper contains a general solution of the problem (plane as well as three-dimensional) concerning the determination of stress taking place just at the moment when a load $p(\xi, \eta)$, arbitrarily distributed over a certain area D, is applied instantaneously to the surface of soil, bounded by the plane $z = 0$.

In accordance with usual assumptions, we will consider the water, filling the pores of the soil, and the particles of that soil, as absolutely incompressible; the influence of air entrapped in the pore water will also be neglected.

Having made these assumptions we must admit that every change in the volume of the soil mass can take place only as a result of the corresponding outflow or inflow of a certain amount of ground water.

Under this condition, an external load applied to the surface of a soil is taken up, at the moment of the load's application, entirely by the water filling the interstices between the solid particles. An instantaneous field of hydrostatic pressures occurring at that moment in the soil mass gives rise to volume forces, acting upon the solid particles of the soil.

The general equations for these volume forces are

$$X, Y, Z = -\Delta\left(\frac{\partial H}{\partial x}, \frac{\partial H}{\partial y}, \frac{\partial H}{\partial z}\right),$$

where H — a function representing the distribution of hydrostatic head,
Δ — volume weight of water.

* Н. М. Герсеванов, Динамика грунтовой массы (1933).

Due to the volume forces, just mentioned, certain stresses appear in the soil skeleton; these stresses must conform to the following equations of the theory of elasticity (here the signs of stresses are taken reversed, in comparison with the usual practice):

$$\frac{\partial \sigma_x}{\partial x}, \frac{\partial \sigma_y}{\partial y}, \frac{\partial \sigma_z}{\partial z} + \frac{\partial \tau_{xy}}{\partial y}, \frac{\partial \tau_{xy}}{\partial x}, \frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{xz}}{\partial z}, \frac{\partial \tau_{yz}}{\partial z}, \frac{\partial \tau_{yz}}{\partial y} + \\ + \Delta\left(\frac{\partial H}{\partial x}, \frac{\partial H}{\partial y}, \frac{\partial H}{\partial z}\right) = 0, \tag{1}$$

$$\nabla(\sigma_x, \sigma_y, \sigma_z) + \frac{1}{1+\mu}\left(\frac{\partial^2 \Sigma}{\partial x^2}, \frac{\partial^2 \Sigma}{\partial y^2}, \frac{\partial^2 \Sigma}{\partial z^2}\right) + \Delta \frac{\mu}{1+\mu} \nabla H + \\ + 2\Delta\left(\frac{\partial^2 H}{\partial x^2}, \frac{\partial^2 H}{\partial y^2}, \frac{\partial^2 H}{\partial z^2}\right) = 0, \tag{1'}$$

$$\nabla(\tau_{xy}, \tau_{xz}, \tau_{yz}) + \frac{1}{1+\mu}\left(\frac{\partial^2 \Sigma}{\partial x \partial y}, \frac{\partial^2 \Sigma}{\partial x \partial z}, \frac{\partial^2 \Sigma}{\partial y \partial z}\right) + \\ + 2\Delta\left(\frac{\partial^2 H}{\partial x \partial y}, \frac{\partial^2 H}{\partial x \partial z}, \frac{\partial^2 H}{\partial y \partial z}\right) = 0, \tag{1''}$$

where ∇ is Laplace's operator, μ is Poisson's ratio, $\sum = \sigma_x + \sigma_y + \sigma_z$.

The stresses must also satisfy the following boundary conditions:

1) at $z = 0$, the stresses σ_z, τ_{xz}, τ_{yz} must be equal to zero;

2) for points located at infinitely large distances from the origin of coordinates, all components of stresses must be equal to zero.

It is necessary, first of all, to find the function H expressing the distribution of hydrostatic head. The decrease in volume of any element of a soil mass can take place only after the outflow of a corresponding volume of water from the interior of the soil. The outflow can not occur momentarily, but takes some time. At the initial moment, therefore, when an instantaneous load has just been applied, the skeleton of soil may undergo deformations changing the shape of each element of the body considered, but not its volume.

The relative change of volume at any point of the soil skeleton is equal to $\frac{1-2\mu}{E}\sum$. The instantaneous stresses appearing at the initial moment, corresponding to the instantaneous application of external load must, therefore, satisfy the condition $\sum = 0$ (the values of E, and μ being arbitrary).

Adding to one another three equations of Beltrami-Michell of the type (1'), we have:

$$(1-\mu)\nabla\sum + \Delta(1+\mu)\nabla H = 0$$

from which, taking $\sum = 0$, we find that $\nabla H = 0$.

The foregoing shows that the determination of the head function H, can be reduced to the determination of a function, harmonic within the region $z \geqslant 0$ of the half-space, the values of this function inside the region D, and at $z = 0$, are equal to $H_{z=0} = \frac{1}{\Delta} p(\xi, \eta)$, while outside of the region D, and at $z = 0$, they are equal to zero; in addition to this the above mentioned function becomes equal to zero for points at infinity.

The problem here considered represents a particular case of the Dirichlet's problem.

The hydrostatic head function H, satisfying the above enumerated conditions, will therefore be expressed by the well known equation:

$$H = \frac{1}{4\pi\Delta}\int_D\int p(\xi,\eta)\frac{dG}{dn}\,d\xi\,d\eta =$$

$$= \frac{1}{2\pi\Delta}\int_D\int \frac{zp(\xi,\eta)}{[(x-\xi)^2+(y-\eta)^2+z^2]^{\frac{3}{2}}}\,d\xi\,d\eta. \qquad (2)$$

For plane problem, the above equation for the H function can be written thus:

$$H = \frac{1}{\pi\Delta}\int_{-a}^{+a} p(\xi)\frac{z}{(x-\xi)^2+z^2}\,d\xi. \qquad (2')$$

The same results can be, of course, obtained after the integration of the equations derived by N. M. Guersevanov, for the H function, for cases of concentrated and linear loads.

Turning now to the determination of stresses in a soil skeleton, we will seek to express them in the following form:

$$\left.\begin{aligned} \sigma_x, \sigma_y, \sigma_z &= z\left(\frac{\partial^2\varphi}{\partial x^2}, \frac{\partial^2\varphi}{\partial y^2}, \frac{\partial^2\varphi}{\partial z^2}\right), \\ \tau_{xy}, \tau_{xz}, \tau_{yz} &= z\left(\frac{\partial^2\varphi}{\partial x\partial y}, \frac{\partial^2\varphi}{\partial x\partial z}, \frac{\partial^2\varphi}{\partial y\partial z}\right). \end{aligned}\right\} \qquad (3)$$

Substituting (3) into $\sum = 0$, we can find that $\nabla\varphi = 0$, that is, the function φ must satisfy the Laplace equation.

Substituting (3) into equations (1), (1′), (1″) and remembering that φ is a harmonic function we obtain:

$$\frac{\partial^2\varphi}{\partial x\partial z}, \frac{\partial^2\varphi}{\partial y\partial z}, \frac{\partial^2\varphi}{\partial z^2} + \Delta\left(\frac{\partial H}{\partial x}, \frac{\partial H}{\partial y}, \frac{\partial H}{\partial z}\right) = 0,$$

$$\frac{\partial^3\varphi}{\partial x^2\partial z}, \frac{\partial^3\varphi}{\partial y^2\partial z}, \frac{\partial^3\varphi}{\partial z^3} + \Delta\left(\frac{\partial^2 H}{\partial x^2}, \frac{\partial^2 H}{\partial y^2}, \frac{\partial^2 H}{\partial z^2}\right) = 0,$$

$$\frac{\partial^3\varphi}{\partial x\partial y\partial z}, \frac{\partial^3\varphi}{\partial x\partial z^2}, \frac{\partial^3\varphi}{\partial y\partial z^2} + \Delta\left(\frac{\partial^2 H}{\partial x\partial y}, \frac{\partial^2 H}{\partial x\partial z}, \frac{\partial^2 H}{\partial y\partial z}\right) = 0.$$

It is easy to notice that all equations in this system will be satisfied if we put

$$\frac{\partial\varphi}{\partial z} = -\Delta H.$$

The stressed state of the soil skeleton, therefore, may be expressed by the following equations:

$$\left.\begin{aligned} \sigma_x &= -\Delta z\int\frac{\partial^2 H}{\partial x^2}\,dz, & \tau_{xy} &= -\Delta z\int\frac{\partial^2 H}{\partial x\partial y}\,dz, \\ \sigma_y &= -\Delta z\int\frac{\partial^2 H}{\partial y^2}\,dz, & \tau_{xz} &= -\Delta z\frac{\partial H}{\partial x}, \\ \sigma_z &= -\Delta z\frac{\partial H}{\partial z}, & \tau_{yz} &= -\Delta z\frac{\partial H}{\partial y}, \end{aligned}\right\} \qquad (4)$$

It will be noticed that a proper value being taken selected for the head function H, the equations of stresses as written above, will also satisfy all boundary conditions mentioned elsewhere in this paper. These equations represent, therefore, a solution of the problem considered.

For a case of plane problem we have:

$$\sigma_x = \Delta z\frac{\partial H}{\partial z}, \quad \sigma_z = -\Delta z\frac{\partial H}{\partial z}, \quad \tau_{xz} = -\Delta z\frac{\partial H}{\partial x}. \qquad (5)$$

Applying equation (5) to particular cases where uniform load on a strip or uniform load extending infinitely in one direction are considered, we can directly get the results identical to ones received by N. M. Guersevanov by another more laborious way.

Equations (2), (2′), (4) and (5) may be represented in another form.

Let us denote ultimate stresses produced in the soil skeleton under the action of the same external load, $p(\xi, \eta)$, by N_x, N_y, N_z; T_{xy}, T_{xz} and T_{yz}.

These stresses are determined from known equations of the theory of elasticity, if hydrodynamical forces are absent. In this case the head function H, at any point of the medium, may be defined as follows:

$$H = \frac{1}{2(1+\mu)\Delta}(N_x + N_y + N_z)$$

or

$$H = \frac{1}{3\Delta}(N'_x + N'_y + N'_z)$$

where the sign denotes the assumption that $\mu = 0.5$. For the case of plane problem:

$$H = \frac{1}{2\Delta}(N_x + N_z).$$

The accuracy of the above statements may be verified by a direct comparison of equations (2) and (2′) with equations for the sums of ultimate normal stresses. Equations expressing initial stresses in the soil skeleton in terms of ultimate stresses are as follows:

$$\sigma_x = N'_x - \Delta H = \frac{1}{3}(2N'_x - N'_y - N'_z), \quad \tau_{xy} = T_{xy},$$

$$\sigma_y = N'_y - \Delta H = \frac{1}{3}(2N'_y - N'_x - N'_z), \quad \tau_{xz} = T_{xz},$$

$$\sigma_z = N_z - \Delta H = \frac{1}{3}(2N_z - N'_x - N'_y), \quad \tau_{yz} = T_{yz}.$$

In the case of plane problem:

$$\left.\begin{aligned} \sigma_x &= N_x - \Delta H = \frac{1}{2}(N_x - N_z), \\ \sigma_z &= N_z - \Delta H = \frac{1}{2}(N_z - N_x), \end{aligned}\right\} \quad \tau = T.$$

This form of equations may prove very convenient in many cases, because the computation of ultimate stresses can be greatly facilitated by the use of tables and diagrams prepared for that purpose.

Having obtained equations for instantaneous stresses, it is easy to find the corresponding instantaneous strains and displacements. The latter are of substantial importance for a series of problems in soil mechanics, and in particular for problems concerning phenomena of vibration.

Received
22 VII. 1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

PHYSIQUE

LA FRÉQUENCE DES OSCILLATIONS DU GROUPE HYDROXYLE DE L'ALCOOL MÉTHYLIQUE ET SA DÉPENDANCE DE LA DENSITÉ

Par G. S. LANDSBERG, membre correspondant de l'Académie, et S. A. UKHOLIN

Le caractère spécifique de la structure de l'eau, noté particulièrement par Bernal et Fowler, la rend au plus haut dégré intéressante comme objet d'étude des forces inter-moléculaires qui se manifestent en une variation de la fréquence propre du groupe OH.

L'étude approfondie de l'effet qu'a la variation de la densité de l'eau sur son spectre de combinaison a suscité l'intérêt pour l'étude d'autres liquides, contenant également le groupe OH. Le liquide qui ressemble le plus à l'eau sous ce rapport est l'alcool méthylique, bien que la substitution d'un hydrogène par un groupe méthylique non-polaire altère la symétrie de la molécule et communique à l'alcool méthylique un caractère moléculaire plus prononcé.

En conséquence, il n'y a pas de raison de supposer que l'alcool méthylique exhibe également dans sa structure une multiplicité complexe si caractéristique pour l'eau. Cette circonstance se fait aussi sentir dans le spectre de combinaison de l'alcool méthylique.

Les oscillations dans le groupe hydroxyle se révèlent, de même que dans le cas de l'eau, par une large bande, située à la même place, mais plus étroite et privée des trois maxima caractéristiques pour l'eau. Il est évident qu'ici également on a affaire à une distortion de l'oscillation propre du groupe OH sous l'influence du champ des molécules voisines.

Il était intéressant d'étudier le spectre de molécules isolées de l'alcool méthylique et la transition de l'état liquide à l'état vaporeux. L'étude était effectuée dans des tubes capillaires à parois épaisses; le spectre de l'alcool méthylique liquide et vaporeux était étudié à diverses températures et pressions, correspondant aux densités: $\delta=0.78$, $\delta=0.76$, $\delta=0.71$, $\delta=0.66$, $\delta=0.57$, $\delta=0.27$, $\delta=0.07$, $\delta=0.04$, $\delta=0.03$, $\delta=0.015$. Les résultats des expériences démontrent que, lorsque la densité de l'alcool méthylique liquide décroît, le maximum qui correspond à la bande OH se déplace de $\nu=3402$ cm^{-1}, quand $\delta=0{,}78$, à $\nu=3535$ cm^{-1}, quand $\delta=0.57$. Il faut signaler que le déplacement du maximum n'entraîne pas ici de variation de la largeur de la bande comme dans le cas de l'eau, où l'on peut observer une diminution sensible de la largeur de la bande.

Certainement, cela s'explique, en partie, par la différence dans la complexité de la structure mentionnée plus haut. Néanmoins, pour l'eau à 200° C, lorsque la structure se simplifie à ce qu'il parait en un «emballage serré» de

molécules, l'échauffement au-delà de cette température n'entraîne pas de déplacement du maximum, si caractéristique pour l'alcool méthylique.

Le second point, où la différence est sensible, est que dans le spectre de l'alcool méthylique encore liquide à $t=190°C$ et $\delta=0.577$ on observe, en même temps que cette bande, l'apparition d'une raie étroite, caractérisant les molécules isolées.

Il est évident que cette circonstance est liée avec le caractère asymétrique de la molécule CH_3OH. Tandis que dans l'eau à densité suffisante l'orientation est toujours telle que l'hydrogène d'une molécule se trouve dans le champ d'action de l'oxygène d'une autre molécule, il peut y avoir dans l'alcool méthylique des dispositions où à côté de l'hydrogène se trouve le groupe non-polaire CH_3 qui n'influe que peu sur la fréquence des oscillations de l'hydrogène. Par conséquent, le groupe hydroxyle se trouve suffisamment isolé de l'influence perturrbante de l'oxygène de la molécule voisine, même quand la densité correspond encore à l'état liquide*.

Il se peut tout de même qu'une telle orientation des molécules de l'alcool méthylique, plus désordonnée, qui est observée à 190° C, correspond à la des-

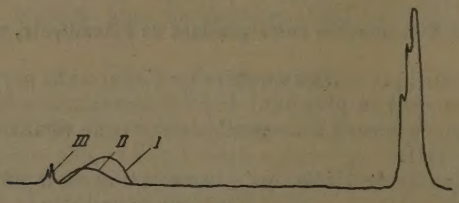

Figure composée d'après les microphotogrammes de l'alcool méthylique liquide et gazeux

I—alcool méthylique liquide à $t=20°$ C et $\delta=0.78$;
II—alcool méthylique liquide à $t=190°C$ et $\delta=0.57$;
III—alcool méthylique gazeux à $t=200°C$ et $\delta=0.04$.

truction des groupes sybotaxiques de S. W. Stewart. Il serait intéressant d'étudier à ce point de vue, à l'aide des rayons *X*, l'alcool méthylique à 190° C et au-delà.

Lorsqu'on approche de l'état critique, la bande devient presque imperceptible, tandis que la raie s'accentue et se déplace quelque peu, tendant vers la fréquence des molécules isolées. Pour l'état gazeux, à mesure que la densité décroît, le déplacement de la raie continue (de 4—5 cm^{-1}), et à $\delta=0.0318$ on atteint la fréquence définitive qui ne varie plus lorsqu'on continue à diminuer la densité. De même que dans le cas de l'eau, la raie correspondant à des molécules isolées consiste en deux composantes:

Une certaine augmentation de la fréquence du groupe hydroxyle dans une molécule isolée d'alcool méthylique, par rapport à une molécule isolée d'eau, $\Delta\nu_1=3639$ et $\Delta\nu_2=3653$ cm^{-1}, décèle l'effet de la substitution de H par le groupe CH_3.

Le tableau et la figure, obtenue d'après les microphotogrammes des spectres, donnent un aperçu complet des variations de la fréquence des oscillations du groupe hydroxyle avec la variation de la densité de l'alcool méthylique. On voit que l'aspect des variations, caractéristique pour le cas de l'eau, est en général vérifié, bien qu'il y ait une série de particularités, liées avec la structure différente des deux liquides et de leurs molécules.

* Les expériences encore non publiées de Landsberg et Malychev ont donné des résultats analogues dans lesquelles l'augmentation de la distance entre les molécules était obtenue par la formation des dissolutions convenables.

Dépendance du spectre de combinaison de l'alcool méthylique de la température t et de la densité δ

Raies excitantes $\nu_1=27\,388\ cm^{-1}$, $\nu_2=27\,353\ cm^{-1}$, $\nu_3=27\,293\ cm^{-1}$

$t°C$	δ	$\Delta\nu$ en cm^{-1}	
20	0.78	3402	
50	0.76	3427	
100	0.71	3473	
140	0.66	3507	
190	0.57	3535	
260	0.27	3670	Etat critique. Raie
220	0.07	3672	
200	0.04	3672 3684	
190	0.03	3672 3684	
160	0.015	3672 3684	

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Manuscrit reçu
le 2. VIII. 1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

PHYSIQUE

DÉPENDANCE DU SPECTRE DE COMBINAISON DE L'EAU DE LA DENSITÉ ET DE LA PRESSION

Par S.A. UKHOLIN

(Présenté par L. I. Mandelstam, de l'Académie, le 2. VIII. 1937)

L'étude de la fréquence des oscillations de l'hydrogène dans le groupe hydroxyle peut servir de méthode sensible pour l'investigation des forces intermoléculaires. On sait en effet que le spectre de combinaison de l'eau liquide est caractérisé par une bande large et diffuse (jusqu'à 600 cm^{-1} de largeur, avec trois maxima—à 3215 cm^{-1}, 3435 cm^{-1} et 3580 cm^{-1}), tandis que l'étude de l'eau à l'état vaporeux révèle pour le groupe OH une raie nette (plus exactement, un doublet étroit avec les fréquences 3639 cm^{-1} et 3653 cm^{-1}).

Le déplacement et l'estompement de cette raie sont indubitablement dus à l'influence des groupes hydroxyles voisins. La grandeur de cette influence dépend de la distance séparant les molécules, les variations de l'aspect de la bande OH décèlent des changements dans la disposition des groupes hydroxyles.

Bernal et Fowler, dans leurs travaux bien connus sur la structure de l'eau, trouvent qu'il est possible de lier la présence de trois maxima dans la bande hydroxyle de l'eau avec les trois structures possibles de l'eau liquide (structure du type de la glace-tridymite, du type de quartz et du type de «l'emballage serré»), dont l'existence est suggérée par les études à l'aide des rayons *X*. L'un des arguments cités en faveur de cette hypothèse est la variation de l'intensité relative des maxima de la bande de l'eau lors de la variation de la température (de 2 à 98°C), ce qui permet de supposer qu'à mesure que la température s'élève, la première structure s'effrite graduellement, tandis que «l'emballage serré» commence à prévaloir. Néanmoins, l'échauffement de l'eau jusqu'à 100°C ne donne qu'une variation minime de la densité de l'eau et, par suite, de la distance entre les molécules. Par conséquent, les effets de l'action inter-moléculaire varient relativement peu, ce qui ne s'exprime qu'en de faibles variations de l'aspect du spectre de la diffusion de combinaison.

Le problème que nous nous sommes posé consistait à étudier ces effets en variant le plus possible les conditions extérieures (la température et la pression), tout en s'efforçant d'observer la transition du spectre diffus, caractéristique pour l'eau liquide, au spectre à raies des molécules d'eau pratiquement isolées.

Ne s'attardant pas à la description de la méthode employée, notons seulement que l'eau étudiée était placée dans des tubes capillaires de quartz

à parois épaisses, permettant d'obtenir des pressions jusqu'à 230 atm. et d'observer, par conséquent, tous les stades de la transition de la phase liquide en vapeur, en passant par l'état critique. Les difficultés considérables de l'étude dans les tubes minces (lumière provenant des parois) étaient partiellement écartées à l'aide des filtres convenables, dont l'usage était rendu facile grâce à la grande fréquence du groupe OH.

Les résultats de l'étude sont les suivants:

Au fur et à mesure de l'échauffement de l'eau la bande du spectre de combinaison se rétrécit quelque peu.

Cela a lieu principalement par suite d'un affaiblissement du premier maximum (3200 cm^{-1}), dont l'existence s'explique, d'après Bernal et Fowler, par la présence d'eau *I* (structure de la glace-tridymite). D'accord avec les observations d'autres auteurs, ce stade correspond donc à la destruction de l'eau *I*. Il se termine pratiquement quand l'eau est échauffée de quelques dizaines de dégrés. Lorsqu'on poursuit l'échauffement, la bande continue à se rétrécir et le centre de gravité du noircissement se déplace graduellement vers le domaine de fréquences plus élevées, tandis que les deux maxima présents se fondent graduellement en un seul. Ce processus se termine pratiquement à $t=200°$ C environ, et lorsqu'on dépasse cette température, l'on n'observe plus qu'un léger rétrécissement de la bande, la position de son centre de gravité restant immuable.

Si l'on s'en tient au point de vue de Bernal et Fowler, l'on doit reconnaître que, lorsque l'eau s'échauffe, sa structure continue à se simplifier, passant évidemment à «l'emballage serré» qui prévaut à haute température et caractérise le liquide idéal. Il faut toutefois noter que l'interprétation proposée par Bernal et Fowler, selon laquelle le maximum 3400 cm^{-1} correspond à l'eau *II* (type du quartz) et le maximum 3600 $cm.^{-1}$—à l'eau *III* (l'emballage serré), semble assez douteuse. En tous cas, le seul maximum qui existe à $t=200°C$ et au-delà, et qui correspond apparemment à l'emballage serré, a la fréquence $\Delta\nu=3530$ cm^{-1}, ce qui diffère sensiblement du troisième maximum de l'eau à basse température ($\Delta\nu=3580$ cm^{-1}). Ce seul maximum subsistant n'est pas le résultat du déplacement graduel de l'un des maxima de l'eau froide, mais apparemment se développe graduellement, tandis que simultanément les deux premiers s'atténuent. Toutefois, un tableau exact du développement de ce maximum ne peut être donné jusqu'à présent, car les photogrammes n'ont pas encore subi une analyse quantitative. On peut néanmoins affirmer que l'interprétation donnée aux maxima $\Delta\nu=3400$ cm^{-1} et $\Delta\nu=3600$ cm^{-1} comme dus aux eaux *II* et *III* ne semble pas fondée.

Si l'on poursuit l'échauffement de l'eau jusqu'à la température critique et au-delà, la densité décroît d'une façon très prononcée (de $\delta_{200}=0.86$ à $\delta_{crit}=0.33$). Le rétrécissement de la bande continue, mais il est minime, de sorte que le passage par le domaine critique, ou la densité décroît rapidement, n'a rien qui le distingue au point de vue des variations du spectre de combinaison. Si la densité continue à décroître et l'eau passe à l'état de vapeur surchauffée, la bande large se laisse encore observer.

Enfin, si la densité tombe à $\delta=0.096$ (la pression est de 135 atm. environ), on commence à distinguer une raie nette de fréquence $\Delta\nu=3646$ cm^{-1}, la bande subsistant encore; cette raie est caractéristique pour la vapeur à basse pression, c'est-à-dire pour les molécules d'eau isolées. On a apparemment affaire dans ces conditions à l'apparition en quantité sensible de molécules pratiquement isolées qui existent simultanément avec les molécules dont l'interaction est considérable. Autrement dit, le temps pendant lequel ces molécules se trouvent hors de la sphère d'action des molécules voisines est comparable au temps nécessaire à l'acte de diffusion de combinaison.

Si la densité décroît encore, le rôle des molécules «isolées» devient plus

important et quand $\delta=0.055$ (la pression est de 100 atm.), la bande pratiquement disparaît et le spectre ne consiste qu'en une raie légèrement élargie, avec la fréquence $\Delta\nu=3646$ cm^{-1}.

Le tableau ne change que peu si la densité continue à diminuer ($\delta=0.04$, $p=75$ atm.; $\delta=0.025$; $p=50$ atm.; $\delta=0.0135$, $p=25$ atm.; $\delta=0.007$, $p=12$ atm.). La raie devient encore plus nette, ce qui permet de constater qu'elle est double, avec les composantes $\Delta\nu_1=3639$ cm^{-1} et $\Delta\nu_2=3653$ cm^{-1}. Dans les limites de précision des mesures (environ ± 4 cm^{-1}) la largeur des raies et leur position restent constantes. Les valeurs $\Delta\nu$ sont très proches des valeurs: $\Delta\nu_1=3646$ cm^{-1}, $\Delta\nu_2=3653.9$ cm^{-1}, trouvées par Rank pour $p=2$ atm.

On peut donc estimer, qu'à partir de la densité $\delta=0.06$ (ce qui correspond à une distance moyenne de 8Å entre les molécules), les molécules de la vapeur d'eau sont si isolées les unes des autres, que la fréquence des oscillations de l'atome d'hydrogène est déterminée par le champ de l'oxygène appartenant à la même molécule et ne dépend pas de l'action de l'oxygène des molécules voisines. Cela ne signifie pas, naturellement, que les molécules n'agissent pas du tout entre elles. L'équation de la vapeur d'eau est encore très différente, sous

Figure composée d'après les microphotogrammes de l'eau et de la vapeur d'eau
I—Eau liquide à $t=60$°C et $\delta=0.98$;
II—Eau liquide à $t=260$°C et $\delta=0.78$;
III—Vapeur d'eau à $t=200$°C et $\delta=0.007$.

ces conditions, de l'équation d'un gaz idéal et les forces agissant entre les molécules sont, par conséquent, encore sensibles. Néanmoins leur influence est relativement minime et ne peut évidemment pas soutenir la concurrence avec les forces intra-moléculaires.

Nos expériences démontrent donc que, lorsque la densité de l'eau diminue, et que, par conséquent, la distance moyenne entre les molécules augmente, la diminution des forces inter-moléculaires exerce distinctement son influence sur l'aspect du spectre de l'eau. Quand la densité de l'eau varie de 1 à 0.06, la distance moyenne augmente de 3—4 à 8 Å et conformément la bande diffuse commence à céder la place à la raie étroite. Quand la distance moyenne dépasse 10 Å, le spectre correspond à des oscillations de molécules pratiquement isolées.

Le tableau ci-dessous représente en chiffres le processus décrit plus haut. Il rend quelque peu schématiquement le phénomène, car seules les positions des fréquences correspondant au maximum d'intensité y sont données. On peut mieux se faire une idée de l'aspect général du spectre, et de ses variations pendant l'échauffement, à l'aide de la figure, composée d'après les microphotogrammes.

Les spectres correspondants étaient excités par le groupe $\lambda=3650$ Å, $\lambda=3655$ Å et $\lambda=3663$ Å. Dans la phase liquide, les bandes provenant de toutes ces raies se fondent en une seule bande large, qui se rétrécit graduellement à mesure que la température s'élève; dans la phase vaporeuse, quand la densité est suffisamment réduite, on peut voir nettement trois raies isolées, satellites des trois raies excitantes, et l'on peut même distinguer qu'elles se scin-

dent en deux composantes. Ces détails sont encore plus distincts directement sur les clichés des spectrogrammes.

Dépendance du spectre de combinaison de l'eau et de la vapeur d'eau de la température t et de la densité δ

Raies excitantes $\nu_1=27\,388\ cm^{-1}$, $\nu_2=27\,353\ cm^{-1}$, $\nu_3=27\,293\ cm^{-1}$

t°C	δ	$\Delta\nu$ en cm^{-1}	
60	0.98	3448	
130	0.93	3497	
200	0.86	3524	
260	0.78	3520	
300	0.70	3530	
320	0.66	3528	
350	—	3530	
380	0.33	3530	État critique
360	0.133	3530	
350	0.096	3530	Bande
		3646	Raie
330	0.055	3646	Raie, bande absente
310	0.025	3645	
250	0.0135	3639	
		3653	
200	0.007	3639	
		3653	

Ce travail a été effectué sous la direction de. G. S. Landsberg, membre correspondant de l'Académie.

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Manuscrit reçu
le 2. VIII. 1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

PHYSICS

ON THE MECHANISM OF LUMINESCENCE IN LIQUIDS UNDER ULTRASONIC TREATMENT

By V. L. LEVŠIN (Lewschin) and S. N. RŽEVKIN (RSCHEVKIN)

(Communicated by S. I. Wawilow, Member of the Academy, 22. VII. 1937)

Luminescence of water produced under ultra-sonic action was first discovered by H. Frenzel and H. Schultes (1). Later, E. Flosdorf, L. Chambers and W. Malisoff (2) observed luminescence produced by sonic frequencies in alkali solutions of the hydrazide 3-aminophtalic acid. After removal of dissolved oxygen by boiling under vacuum and saturation of the water with nitrogen no luminescence was observed. L. Chambers (3) found that besides water, luminescence, of less intensity, is also observed in other liquids, of which it is most intense in nitrobenzene. Chambers states that the intensity of luminescence varies inversely as the temperature. According to his view, luminescence appears as a result of the distortion of the quasi-crystalline structure of the liquid under ultra-sonic action; this process is analogous to tribo-luminescence in crystals.

For the study of ultra-sonic luminescence we used a quartz plate $4\times22\times37$ mm with a cut parallel to the electrical axis, frequency of resonance $f=525$ kHz fed by a high-power generator (1.5 kW in the oscillatory circuit, potential difference on the quartz plate up to 5000 V). The quartz plate was placed in a vessel with transformer oil, on a copper diaphragm (0.02 mm) under which there was an air-filled cavity; above it was slightly pressed by a similar diaphragm; a high-frequency difference of potential was impressed between the diaphragms. Ultra-acoustic vibrations were transmitted by the oil to the bottom of the vessel.

The oil was cooled with a coil-pipe with running water. The intenisty of luminescence was measured by means of a wedge photometer, radioactive phosphorus serving as a field of comparison. The observation of luminescence in liquids was made in a dark room. Luminescence in water could be observed in a few minutes after adaptation.

1. The general course of the phenomena. Most simply the phenomena proceed in small columns of a liquid ($d\approx3$; $h\approx5$ cm). Luminescence is produced at the bottom of the vessel or, less often, appears from above in the form of a narrow band. It gradually becomes more intense, and widens, filling, finally, the entire vessel. This gradual increase of brightness is, however, interrupted sometimes by a sudden abrupt intensification of light. Having fully developed, luminescense remains permanent for some time, then becomes fainter, and finally vanishes in an abrupt way, a specific noise aris-

ing in the liquid. We see, therefore, that five phases can be traced in the luminescence phenomenon, namely: 1) gradual growth, 2) abrupt intensification, 3) permanent intensity, 4) gradual decline and 5) an abrupt breaking-off. The duration, however, of the different phases varies greatly, and not infrequent are cases when some of them are absent altogether. When water is for the first time subjected to sonic treatment, luminescence is always very faint in the beginning and brightens gradually, while in repeated treatments of water, as well as of concentrated solutions NaCl, $CaCl_2$ and H_2SO_4, luminescence of full intensity is produced at once. In 24 hours after sonic treatment water acts as if it were not subjected to treatment.

The breaking-off of luminescence at the end is mainly associated with the warming of the liquid. In vessels provided with a cooler the liquid can emit light for a very long time. In small, quickly warming columns of water the entire process lasts a few seconds, while in large columns, 30—40 cm long, luminescence lasts a long time. For instance, in water volumes of 5, 15 and 40 cm^3 the duration of luminescence was 10, 44 and 148 seconds respectively.

Table 1

Influence of Temperature on the Intensity of Luminescence

Water subjected to triple distillation		Top-water		Water with hydrazide		Aqueous solution NaCl 20%		H_2SO_4 with a small amount of water	
$t°$	I	$t°$	I	$t°$	I	$t°$	I	$t°$	I
10	1.0	—	—	—	—	—1	0.4	24	0.4
20	1.0	—	—	24	1.0	6	0.8	65	0.8
30	1.0	32	1,0	31	0.7	20	1.0	97	1.0
40	1.0	44	1,0	42	0.5	27	0.8	145	0.6
45	0.6	48	0,6	48	0.4	38	0.8	—	—
54	0.4	50	0,6	—	—	43	0.9	—	—
Breaking-off		Breaking-off		Breaking-off		Breaking-off			

In our experiments luminescence broke off at about 50° C. After vanishment of luminescence, with the intensity of excitation decreased by the detuning of the oscillatory circuit, it re-appeared for a short time. The temperature of the breaking-off in solutions of substances with a high power of absorbing water vapor ($CaCl_2$ and H_2SO_4) is much higher (Table 1 and Fig. 1).

In long tubes the process is more complex. Straight (30—40 cm) and bent (up to 1.5 m) tubes were studied. Luminescence does not fill the whole volume but is concentrated at the bottom, or at the air limit of the liquid. An air bubble in a bent tube can also serve as such a limit. Both at the bottom, at the oscillator, and at the top, at the surface of liquid, luminescence is stable; at intermediate points it appears in separate pieces, gradually, but sometimes very quickly, moving upwards. Instantaneous swift upward movements of luminescent clouds were also observed. In not very long tubes the luminescent clouds not infrequently reach the liquid surface, but sometimes they disappear on the way. In very long tubes no clouds were observed beyond 40 cm from the bottom of the vessel. At the time of the ultra-sonic treatment of the tube in light, in different places of the tube were observed a violent production of bubble volleys and the appearance of clouded spots shifting upwards at a speed approaching that of the shifting luminescent clouds.

2. Nature of luminescence. The object of the experiments was to find the source of luminescence and means of its excitation. Luminescence may be exhibited by a) the liquid treated, b) slightest impurities in it, c) gases liberated by the liquid during its being treated by sonic action. Luminescence may be produced by chemical processes or by excitation with an electric discharge. The latter process may be produced in minute cavities under the action of an external or an internal electric field, while the former is more probable in liquid media. In order to elucidate the nature of luminescence the following experiments were carried out:

1) To treatment by sonic action were subjected: water; ethyl, propyl and isobutyl alcohols; glycerine; benzene; xylol; 4-chlorocarbon; nitrobenzene and sulphuric acid. Of these liquids, water invariably exhibited luminescence. Luminescence of concentrated sulphuric acid ($>95\%$) was feeble and decreased in intensity and duration with the decrease in the content of water; in glycerine there was observed a long but extremely weak luminescence. Luminescence of these two liquids apparently may be explained by the presence of a certain amount of water in them. The other liquids, including nitrobenzene, did not exhibit luminescence.

2) In order to elucidate the influence of impurities, in particular those which produce blue photoluminescence in all, even «pure», liquids, luminescence of water taken from the water-supply was compared with that of water which had undergone distillation four times, no blue photoluminescence being produced in the latter. After numerous experiments it was established that the above difference keeps within the limits of reproducibility of each experiment.

Besides the experiments with distilled water, the absence of influence of photoluminescent substances was also confirmed by experiments in which distilled water and alcohols were contaminated by adding typical fluorescent substances: rhoduline, rhodamine and uranyl-sulphate. In alcohol solutions of these substances no luminescence was observed, while in aqueous solutions luminescence was as intense as in ordinary water.

3) In order to determine the role of dissolved gases, particularly that of oxygen, their content was reduced a) by a continuous boiling of the water, b) by boiling with the simultaneous treatment with nitrogen, c) by adding pyrogallol. The first two treatments did not bring about any decrease in luminescence of water: on the contrary, luminescence in boiled water was found to be somewhat more intense. Addition of the first portions of pyrogallol produces a slight effect, while in 10% solutions luminescence sharply becomes fainter but does not vanish.

4) In order to elucidate the question where luminescence takes place (liquid or gaseous phase) experiments were conducted with typical luminescence quenchers, in the liquid and gaseous medium, such as KI, pyrogallol, CO_2 and $NaHCO_3$. The first two quenchers in concentrations, causing a violent quenching of photoluminescence in liquids, produce but a very slight effect in quenching of acoustic luminescence. Their action is more or less apparent in high concentrations and, in case of pyrogallol, is to a considerable extent the result of the yellowing of the solution.

Influence of Quenchers

Table 2

	KI		Pyrogallol				$NaHCO_3$				
C g/g	0	0.2	0.0	0.015	0.05	0.10	0	0.0003	0.0012	0.007	0.07
I	1.0	0.9	1.0	0.50	0.25	<0.16	1.0	1.0	0.47	0	0

A strong quencher of gases—CO_2—was also found to be a very strong quencher of acoustic luminescence both in water and H_2SO_4.

The above experiments show the cavitation nature of the process. As shown by Rayleigh (4), when a small cavity in the liquid, filled with the gas, is suddenly compressed, exceedingly high pressures may develop in the liquid, at the surface of the cavity. According to Rayleigh's formula, when a bubble is compressed to $^1/_{20}$th of its volume, there arises a pressure of about 10 000 atm. Resulting from such a process are hydraulic shocks, the strong action of which is manifested in narrowly limited volumes of the liquid; they produce, for instance, the corrosion of metals. It may be assumed that when the bubble is annihilated high electric potentials are formed within a small volume of the liquid. High electric potentials may likewise be expected to arise during the very formation of cavities as a result of the drop of pressure up to negative values, in the process of violent ultra-sonic vibrations, the amplitude of pressure in which may reach several atmospheres (5). In the resulting rupture an electric discharge takes place by which the vapor filling the cavities is excited.

The absence of influence of small impuritie (experiments 2) as well as the slight influence of KI is easily explained by their being present in the

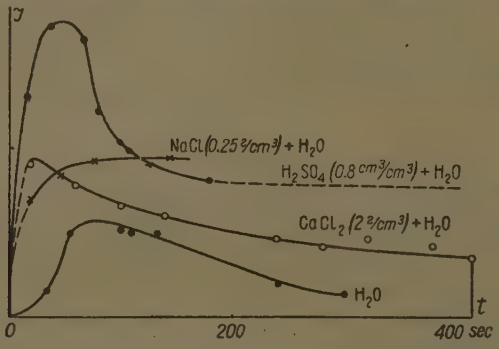

Fig. 1.

liquid phase, while the quenching action of CO_2 manifests itself, in view of its penetration into the cavities. The experiments (1) and (3) lead us to the assumption that the vapor in which the luminescence was observed was merely the vapor of the water. Furthermore, the decrease of the luminescence intensity, as shown in Table 1, with the rise of temperature, is, also, to be explained by the increase of pressure of the vapor with the rise of temperature, and the worsening of the discharge conditions.

Taking as a basis the cavity stand point, we performed a number of experiments in order to decide the question: is the discharge inside the cavity due to the influence of the external field of the generator, or it is the result of the formation of internal fields at the moment of formation or annihilation of the cavity. Both the additional field of the induction coil and the decrease of the external field by imposing screening metallic plates did not affect the intensity of luminescence. This result fully corresponds to the data obtained by Frenzel and Schultes (l. c.) who also failed to detect any influence of the screening of the field. It appears, therefore, more probable that the discharge is due to the action of the internal fields. The latter, however, can produce a discharge either between two parts of an insulator or between two disconnected conductors. An addition of considerable amount of NaCl to distilled water not only failed to annihilate luminescence but

raised its intensity (Fig. 1). It follows, therefore, that the discharge probably takes place between the walls of the bubble and the minute sprinklings of water formed inside the bubble at the rupture or annihilation of the cavity.

From the point of view of the cavity theory the decrease of the vapor pressure inside the cavity should be regarded as favouring the production of the discharge. This has been verified in luminescence of the solutions $CaCl_2$ and H_2SO_4 which was produced at the temperatures up to 60 and 140° C respectively.

Although the cavity theory of luminescence provides sufficient ground for the interpretation of the principal facts observed, it cannot, however, be considered as being fully established, since many details of the process have not yet been elucidated. The gradual, very slow development of luminescence in water when it is first subjected to sonic action, as well as an instantaneous production of luminescence in repeated treatements, proceed in such a way as if the luminescence appears only through a preliminary formation of a certain substance. The fact that in running water luminescence may last for an indefinitely long time but its intensity is not high, is in full accord with the

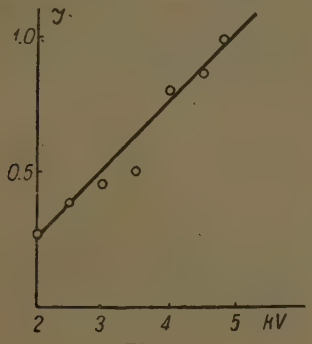

Fig. 2.

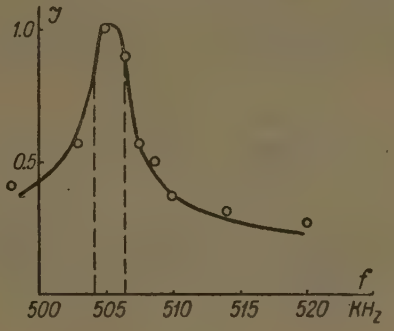

Fig. 3.

above observation. The action of salts in presence of which luminescence instantaneously arises is also obscure.

3. Experiments with Hydrazide. It is known that this substance being oxidized in alkaline media produces blue luminescence. An addition of hydrazide to water treated with sonic action produced light luminescence. Sonic treatement of water containing hydrazide produces bright luminescence. All the above mentioned experiments apply also to water containing hydrazide. In this case, however, luminescence is of much greater intensity. In non-aqueous solutions in which no luminescence is produced hydrazide is also non-luminescent. The close parallelism of luminescence in hydrazide and aqueous solutions is disturbed, however, by their behaviour towards quenchers. Acoustic luminescence of hydrazide is quenched by pyrogallol which is quite natural as the process proceeds in the liquid phase. It follows from the parallelism of the above two luminescences that luminescence of water is produced under the influence of the same process under which active oxygen, or H_2O_2, is formed.

Experiments with hydrazide were carried out for various intensities of excitation. Change in intensity may be attained by changing the distance from the bottom of the vessel to the source of vibrations, the potential difference of the field and the tuning of the oscillatory circuit.

With the change of the distance between the bottom of the vessel and the membrane, periodic changes in intensity of luminescence occur which are

associated with the bottom of the vessel getting into nodes and pencils of the respective stationary waves. When the bottom of the vessel touches the surface of the oil (in a calm state) stable luminescence is produced; when, however, the bottom of the vessel is placed at some distance from the surface of the oil, in such a way that its washing could take place only when a fountain is formed in the liquid, luminescence is of intermittent nature, and formation of clouds is then observed.

In the first approximation there is a linear dependence of luminescence intensity upon the potential difference (Fig. 2), and a sharp resonance maximum is observed on tuning (Fig. 3). In violent vibration luminescence vanishes, and instead of a continuous curve (Fig. 3) the dotted part which is not clear from the theoretical point of view, is formed in the center. It appears from the above that the formation of cavities can only take place at an entirely fixed regime inside the liquid. A study of luminescence may yield ample data regarding the regime of the liquid when acoustic waves are passing through it, as well as of the rate of formation of H_2O_2.

On the basis of the results obtained from the present work we think that the most adequate explanation of acoustic luminescence is the formation of cavities inside the liquid, filled with water vapor, which is excited and produces luminescence under the influence of potential differences which are produced when the liquid is disrupted or the cavities are annihilated.

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Received
22. VII. 1937.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

GEOPHYSICS

SPECIFIC ELECTRICAL RESISTANCE OF FROZEN SOILS

By A. T. AKIMOV

(Communicated by A. D. Arkhangelskij, Member of the Academy, 29. V. 1937)

The exploration of the northern regions undertaken in our country as one of the most urgent tasks, is getting more active and profound from year to year.

The greatest part of the northern regions remains permanently frozen and, therefore, a thorough exploration of the northern regions is only possible alongside a study of the conditions of the permanent frozenness. Practical work in the north is going on under very peculiar conditions, indeed, and the methods used in other parts of the globe prove to be inapplicable here. This fact often creates considerable difficulties in the realization of some of the schemes connected with socialist construction and is not infrequently responsible for useless expenditure.

With regard to geological prospecting, the organization of this work on a more economical and effectual basis would call for the use of new geophysical methods. On the other hand, for the proper organization of geophysical investigations in the search for minerals, as well as in solving structural, engineering and other problems, a thorough knowledge of the physical properties of frozen soils, in particular their electrical properties, is indispensable.

A laboratory for the study of the physical properties of frozen soils has been established at the Geological Institute of the Academy of Sciences. Simultaneously with the investigation of the processes taking place in frozen soils for building purposes, which is conducted under the leadership of M. I. Sumgin, the above mentioned laboratory is also engaged in the study of the electrical constant (ε) and of the specific electrical resistance (ρ) of frozen and thawed soils which is one of the principal subjects of its research work. The latter study is being carried on by the author, under the guidance of A. A. Petrovsky.

The study of electrical resistance (ε) was conducted in a frozen box constructed after Beleliubsky, a mixture of ice and salt serving as a cooler, which permitted to reach the temperature of —20° C. A sample of the soil was placed in a metallic box, measuring $24 \times 24 \times 12$ cm, on the upper plate of which was mounted a miniature four-electrode Schlumberger plant.

The measurements were made by the compensation method, by means of a Raps potentiometer permitting to attain great accuracy by elimination of contact resistance and polarization.

The use of the frozen box in the studies offers a great number of unavoidable difficulties, for the overcoming of which a great deal of time was spent

during 1936. At the present time definite results have been obtained from this work.

Three samples representing the most typical soils, viz.: sand, sandy soil and clayey soil were subjected to a study at various degrees of moistening and under various degrees of temperature.

From the theoretical point of view, it would be natural to expect an increase of specific resistance of moistened soils during their transition from the thawed to frozen condition, as ice is regarded as an insulator, while moistened thawed soils have great conductivity.

This has been fully verified by the results of the experiments carried out in 1936. Specific resistance jumps from ρ of the $10^4 \Omega cm^2/cm$ order in thawed

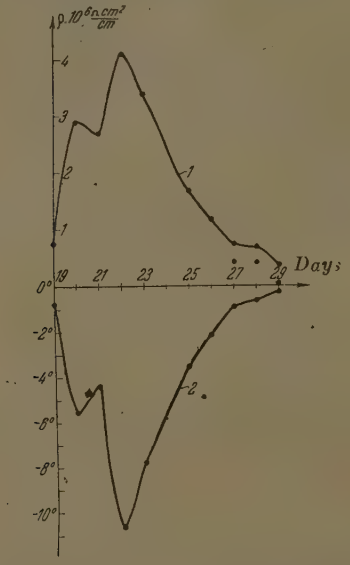

Fig. 1. The curves of the dependence of specific resistance and temperature on the number of days of freezing in the sand: *1*—curve of specific resistance, *2*—curve of the temperature.

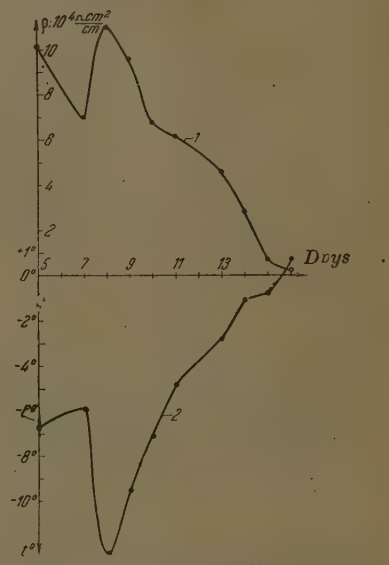

Fig. 2. The curves of the dependence of specific resistance and temperature on the number of days of freezing in the sandy soil: *1*—curve of specific resistance, *2*—curve of the temperature.

condition to ρ of the $10 \Omega cm^2/cm$ order in frozen condition. In some of the soils the jump was still sharper. It was further noted that within frozen condition as well may occur considerable changes of specific resistance due to variation of negative temperature.

The following curves for sand and sandy soil represent the results of the more detailed work carried out with the same soils in the beginning of 1937 (Fig. 1 and Fig. 2) (the curve for clayey soil is not given; it has the same appearance). The samples were taken from fully moistened and moderately condensed soils. The measurement of specific resistance was made without taking the device out of the frozen box. The temperature was measured by means of a four-point thermocouple dipped vertically in the middle part of the sample.

We have thus obtained in the soils four temperature points placed along a vertical line at a distance of 2 cm from each other. The measurement of temperature was made immediately after measurement of specific resistance. The experiment has shown that there is a comparatively small difference in temperature at the four points. The ordinates of the temperature curves

on Fig. 1 and 2 represent each an arithmetical mean of the above mentioned four temperatures measured for each day.

As the frozen box does not keep cold for a long time at a fixed temperature, it was necessary to recharge it in order to be able to continue the experiment. The temperature curves and, correspondingly, the curves of specific resistance show, therefore, several rises and declines, instead of only one. A superficial examination of these curves is sufficient to draw one's attention to the surprisingly distinct reaction of the specific resistance to the change in the negative temperature: the curve of the specific resistance represents a kind of a mirror reflection of the temperature curve*.

The dependence of the curve of specific resistance of sand in frozen condition is more apparent than in sandy and clayey soil, as the processes of freezing in sand are taking place in a more «pure» form than in sandy and, particularly, in clayey soils, where, in addition to the influence of the gravitation water upon the process, there is also a great influence of filmy and capillary water.

Such sharp changes in specific gravity of soils within the bounds of their frozen condition should depend, essentially, on the quantity of water which has not yet been reduced to the solid state. It follows from the above that in frozen soil, even at a sufficiently low temperature, there is a co-existence of water in the solid and liquid phases. A rise or fall of the negative temperature brings about a rise or a fall in the percentage of each of these phases contained in the soil.

In a frozen box it is impossible to closely adjust the temperature in the soil, and our experiment, therefore, has yielded only qualitative results which present a reasonably full confirmation of the theoretical assumptions, but do not yet permit to make any broad generalizations on the basis of quantitative investigations.

The experiments will be continued in a special cooling chamber equipped with refrigerating machines—compressors. The above refrigerating plant is now under construction and will be ready for use within a short time.

This work has yielded results of practical importance. Until recently, specific resistance of rocks in conditions of permanent frozenness had been thought to approach that of ice which means that in their first approximation they should be regarded as dielectrics and that, consequently, work by means of a direct current in frozen rocks is impossible or exceedingly difficult.

Some occasional works in the regions of permanent frozenness have shown that this is not always the case, which is also confirmed by the results of our observations in the laboratory.

It may be assumed, therefore, that at those points of permanent frozenness where the temperature is from 0 to—2° (—3°) work by means of a direct current is possible.

At lower temperatures, however, the use of other methods, e. g. ondometric, may prove to be necessary.

In any case the work should be planned according to the region, it being necessary to take into account not only the temperature of the frozen soil but also other characteristics, such as mineralization of the water and, particularly, their salinity.

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Received
29. V. 1937.

* We think that such relationship between the curves of temperature and specific resistance may serve as a basis for the study of the processes of thawing and freezing at experimental stations, in road building and in making observations of the stability of constructions on permanently frozen soils.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

PHYSICAL CHEMISTRY

ON LINEAR CORROSION OF METALS

SELECTIVE CORROSION OF IRON ACCORDING TO THE SYSTEM: WATER—SULPHURIC ACID—PROPYL ALCOHOL, AT THE BOUNDARY OF THREE PHASES

By L. GINDIN and F. ŠEMIAKIN

(Communicated by M. A. Iljinskij, Honorary Member of the Academy, 28. VII. 1937)

In the first communication of the present series (1) we showed that corrosion of a number of metals partly coated with paraffin, e. g. corrosion of iron by sulphuric acid, is mostly localized at the line of their contact with paraffin and liquid. This enabled us to formulate the concept of linear corrosion, i. e. selective corrosion of metals at the boundary of three phases.

Literature data, as well as our experiments, proved beyond doubt that linear corrosion takes place at the contact of metals with the boundary of not only the solid and liquid phases but also two liquid phases, as well as at the boundary between the liquid and gaseous phases. In other words, the effect of linear corrosion occurs at different combinations of phases of all three aggregate states, e. g. corrosion of metals at the «water-line», which was known long ago. The explanation of the mechanism of this corrosion has been attempted at by a great number of authors. Spring (2), Klobukov (3), Ganguli (4), Hedges (5), Evans (6), and others. As long ago as in 1881, A. Orlovsky (7) described selective, in essence, corrosion of copper at the boundary of two liquid phases. The importance of different forms of polyphase contact in corrosion of metals has been stressed more than once by V. A. Kistiakovsky (8). The experimental data on hand, however, provide a very incomplete characteristic of corrosion at the boundary of three phases, whereas linear corrosion requires a systematic and thorough study, without which its theoretical interpretation is impossible.

Our aim at this stage of the experiments was to elucidate the special characteristics of linear corrosion at the boundary between phases of different aggregate states, and also to study the influence upon this effect of a number of physico-chemical factors, and first of all of the composition of the attacking medium.

We accordingly elaborated a method of the experiments permitting to establish a number of boundary lines of phases, which will be dealt with in a further part of this paper, and studied the action of the three-component system upon iron by means of the Gibbs' triangle method. It is to be mentioned here that the methods of physico-chemical analysis which are being so successfully elaborated by N. S. Kurnakov and his school should be more widely used in the study of corrosion processes with regard to construction of diagrams showing the composition of the alloy and its corrosion resistance

as well as those showing the composition of the medium and its attacking properties.

In the experiments in question we studied corrosion of iron by the system: water—sulphuric acid—primary propyl alcohol*.

Iron «Armco» type, made by the «Serp i Molot» metal works, tape, 0.01 cm thick. Composition: C—0.04%; Si—0.03%; Mn—0.03%; Fe—99.9%. Water, distilled. Sulphuric acid, chemically pure, specific gravity 1.84. Primary propyl alcohol, thoroughly distilled, boiling point, 97°C. Paraffin of Kahlbaum.

The method applied in the experiments was as follows: a molten paraffin was put into a measuring glass, provided with a ground-in cork. The paraffin layer was 1.5 cm thick. Two plates of iron were immersed in paraffin, immediately before its cooling, up to $^1/_3$ of their height, at a distance of 2 cm from each other. The plates of iron had been first treated by the method described in our preceding Note. The size of the plates was 4×2 cm, thickness 0.01 cm. After this, a cooled mixture of the reagents, made up according to weight, was poured upon the layer of paraffin. Each glass was filled with 30 g of the mixture. At the point 5, for instance, the mixture was made up as follows: 6 g acid, 6 g alcohol and 16 g water, total 30 g; at the point 29: 3 g alcohol, 24 g acid and 3 g water, total 30 g, etc. The liquid covered the plate of the metal to about one third of its height, so that the upper third of the plate was raised above the level of the liquid. Two boundary were therefore obtained: air—liquid and liquid—paraffin. All the points along the triangle were twice repeated, new mixtures being made up each time at different points. The experiments lasted 6 days, in isothermal conditions, at the temperature of 20°C.

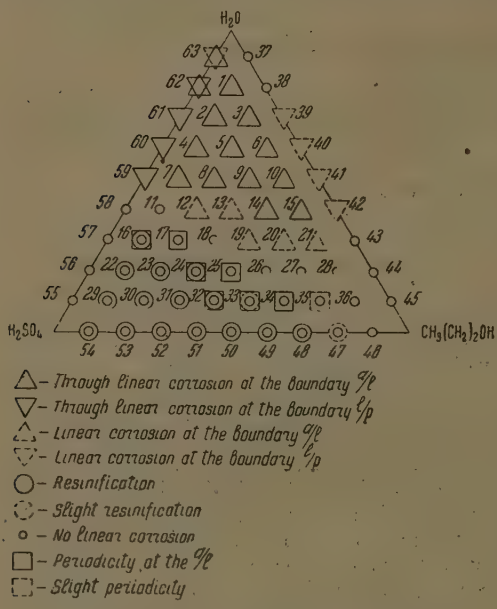

Fig. 1. Iron corrosion by the system: $H_2O—H_2SO_4—CH_3 \cdot CH_2 \cdot CH_2 \cdot OH$

The results of the experiments are given in the Table and are shown on the triangular diagram (Fig. 1).

Discussion of Results

It is, in the first place, the definite dependence of the nature of corrosion on the composition of the attacking medium that attracts attention in the triangular diagram. Of special significance is the existence of a sharply defined area of linear corrosion which is subdivided into sub-areas: linear corrosion at the air—liquid line and at the liquid—paraffin line. Furthermore, the diagram clearly shows the outlines of the area in which on the surface of the

* We intend also to study other members of the homological series of alcohols, as well as other classes of organic compounds.

Table

Corrosion of Iron by the System: Water—Sulphuric Acid—Primary Propyl Alcohol

Numbers of points	Observations
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 14, 15.	At the air—liquid line: through linear corrosion of iron. The upper parts of the plates raised above the level of the liquid fell-off (Fig. 2). Corrosion of the rest of the surface of the metal is comparatively slight
12, 13, 19, 20, 21	The same, but the upper parts of the plates had not fallen-off by the moment of observation as linear corrosion proceeded somewhat slower
16, 17, 24, 25, 32, 33, 34, 35	General uniform slight corrosion. No linear corrosion. On the part of the surface of the metal emerging out of the liquid, from the boundary air—liquid and upwards, there were formed, periodically, films of corrosion products, consisting of thin, wavy strips differing in colour from the rest of the surface (Fig. 3). The direction of the films was, in the main, across the plates. The total number of films was 15—20. The distances between the films gradually increased from the boundary upwards
11, 18, 22, 23, 26, 27 28, 29, 30, 31, 36	No linear corrosion. No periodicity. General uniform slight corrosion
16, 22, 23, 24 29, 30, 31, 32, 33	A darkening of the liquid which was, probably, associated with resinification of the alcohol. A very slight general corrosion of iron. No linear corrosion
37, 38, 43, 44, 45	No linear corrosion. A slight rusting of the metal in the liquid
39, 40, 41, 42	Well-marked linear corrosion at the liquid—paraffin line. Marked rusting of the metal in the liquid
55, 56, 57, 58	Very slight general corrosion. No linear corrosion
59, 60, 61	Very strong corrosion of the iron in the liquid. The plates of the metal were converted into a thin, transparent net (Fig. 4). Through linear corrosion at the liquid—paraffin line. The strongest corrosion is at the point 59 (Fig. 5)
62, 63	Through linear corrosion at the air—liquid line. Linear corrosion at the liquid—paraffin line, through at the point 62 and not through at the point 63. The plate of metal in the liquid at the point 62 was converted into a thin transparent net
46, 47, 48, 49 50, 51, 52, 53, 54	General corrosion is very slight. No linear corrosion. At all points, except point 46, resinification of the liquid was observed. Slight resinification was observed at point 47

metal, above the level of the liquid, periodic formations of some special nature are observed. These formations represent an entirely new type of periodical structures which until now has not been described in literature. It is our intention to study this phenomenon in more detail.

Fig. 2. Through linear corrosion at the boundary air—liquid. Point № 8. × ×1¼ times.

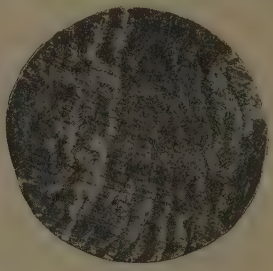

Fig. 3. Periodical films of corrosion products. Point № 17. × 10 times.

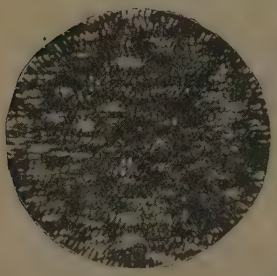

Fig. 4. Iron corrosion at the point № 59. × 55 times.

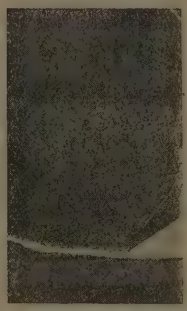

Fig. 5. Through linear corrosion at the boundary liquid—paraffin. Point № 59. ×2 times.

On the diagram is, finally, visible the area in which the darkening of the liquid takes place. This is, probably, associated with the resinification of propyl alcohol or, rather, of the products of the chemical changes it undergoes (e. g. dehydration) under the action of sulphuric acid. In this area general corrosion was the slightest.

In the course of time, however, a certain extension of the outlined areas of general corrosion may take place. It can be seen, therefore, that the entire process as above described is to be assigned to a certain point of time, a characteristic of all systems which have not yet been fully stabilized.

Conclusions

1. In the above described experiments was studied corrosion of iron, «Armco» type, by the system: water—sulphuric acid—primary propyl alcohol, by means of Gibbs' triangle method.

2. A close dependence has been established of the nature of corrosion, in particular its localization at the boundary of the phases, upon the attacking medium.

3. The areas of linear corrosion, periodical structures and resinification have been traced on the triangular diagram.

Received
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
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CHEMISTRY

THE RELATION TO METALS OF SULPHUR SOLUTIONS AND OF A SERIES OF ORGANIC SULPHUR COMPOUNDS IN SATURATED HYDROCARBONS

THE RELATIONS TO IRON OF ETHYL- AND BUTYL-MERCAPTAN SOLUTIONS IN CYCLOHEXANE*

By L. G. GINDIN, I. I. TORSUJEV and V. A. KAZAKOVA

(Communicated by M. A. Iljinskij, Honorary Member of the Academy, 29. VI. 1937)

Of all the thio-compounds contained in hydrocarbon fuel, mercaptans are admittedly the most aggressive ones in relation to metals. A proof of this may be seen, amongst other things, in the fact that up to the present, sodium plumbite has been largely used in the purification of benzines for prophylactic purposes, mainly to prevent corrosion.

There could be no doubt of the fact that mercaptans react readily with such metals as copper, lead, silver, etc. The relation of mercaptans to iron was not, however, quite clear. On this point which is of great practical interest, we had but one testimony, namely, Wood, Sheely and Trusty's (1) statement to the effect that a solution of iso-amyl-mercaptan in «ligroin» after remaining in contact with iron for a month, had not affected it in any way. Important as this testimony is, it is anything but exhaustive in so far as the whole question is concerned. With a view to its further elucidation we have therefore studied the relation to iron of cyclohexane solutions of ethyl- and butyl-mercaptans, some of the first terms of the homologous series of the aliphatic mercaptans usually present in benzines.

Experimental

Ethyl- and primary butyl-mercaptans were synthesized by the action, under certain conditions, of an alcohol solution of potassium hydrosulphide on the respective iodides (2). Dried over calcium chloride [(2), (3) and others], the mercaptans were synthesized by the following constants:

Mercaptan	Boiling point 760 mm °C	Specific gravity $\frac{20}{4}$
CH_3CH_2SH	37.0	0.839
$CH_3(CH_2)_2CH_2SH$	98.0	0.843

* Communication see in C. R. Acad. Sci. URSS, III (XII), N 5 (100), (1936).

Relation to Iron* of Mercaptan Solution in Cyclohexane

№ of experiment	Duration in days	Dynamics of sulphur: Percentage of sulphur in a previously diluted solution after the end of the experiment: According to calculation based upon the initial concentration of the solution	Dynamics of sulphur: Percentage of sulphur in a previously diluted solution after the end of the experiment: According to analysis	Deficiency	Alternation in the weight of specimen	Condition of the surface of the specimen of iron	Remarks
		Relation of ethyl-mercaptan solution to iron Concentration of «mercaptan» sulphur in the solution before it came into contact with the iron, 0.344% (in the sample). Total sulphur content (including the sulphur contained in the solvent), 0.355%. The amount of solution used in every experiment was 17 cm³, making 0.0451 g sulphur as mercaptan					
17	800	0.088 0.075 0.091	0.086 0.076 0.094	None	+0.0005	The surface of all the three specimens is clear and bright	
18	800	0.099 0.097	0.097 0.097		−0.0002		
19	800	0.102 0.085	0.101 0.088		+0.0004		

		Relation of butyl-mercaptan solution to iron «Mercaptan» sulphur in solution, 0.347% (in the sample); together with the sulphur in the solvent, 0.358%. 16 cm³ of solution were used in every experiment, consequently, 0.0431 g sulphur as C_4H_9SH				
13	1020**	0.065 0.086 0.102	0.068 0.088 0.103	None	+0.0003	The surface of the specimen is clear and bright
14		0.097 0.089 0.075	0.099 0.092 0.072	None	−0.0282	The specimen was strewn with isl ts of coating outwardly very similar to rust
15		0.108 0.095 0.089	0.106 0.097 0.089	None	−0.0004	Surface unchanged

After three months of contact of the iron with the solution there was noticeable on the former a fine pattern of a coating very similar to rust. Later on the coating increased. After the main bulk of the coating had been mechanically removed and investigated by the micro-chemical method, the specimen was treated with an anti-rust compound (4) wherein the coating dissolved

* The composition of the iron was stated in our previous article. Although it was referred to as steel in that article, we shall not be far out, judging by its content of carbon, if we describe it as iron.

** Such a duration of the experiments was not, as already stated, due to any special conditions. The experiments drew out in length simply because a long time had elapsed before the writers were enabled to make the necessary tests.

The Kahlbaum cyclohexane used as a solvent for the mercaptans* contained 0.011% sulphur. To remove the latter, the cyclohexane was treated, similarly to the hexane, with a liquid alloy of sodium and potassium(2 : 1).

However, even the heating of the cyclohexane together with the latter in a sealed tube at a temperature above 100° C for thirty hours failed to reduce the sulphur concentration. A sulphur so inert could not, of course, give rise to uneasiness, in so far at least as its direct action upon the metal was concerned.

The cyclohexane (after remaining for 72 hours over the alloy) showed the following constants: boiling point 81°C; specific gravity $\frac{15°}{15°}$, 0.7764; sulphur 0.011%.

The solutions were prepared in the usual manner, i. e. by dissolving the mercaptan specimen (in a phial) in the requisite amount of the hydrocarbon, their content of sulphur upon contact with the metal being determined by the standard lamp method in its volume variant. Since the solutions were prepared in such a manner as to ensure a sulphur content of about 0.5%, while the lamp method, as previously ascertained by the writers, gave reliable results only with sulphur concentrations not exceeding 0.1%, the solutions before burning were diluted with hexane. For this purpose an ordinary dry test-tube was drawn out into a capillary, a capillary funnel being inserted into the latter. The whole was weighed to within the fourth decimal, and the mercaptan solution to be analysed was poured in, the whole was re-weighed, and the mercaptan specimens were diluted with a definite amount of hexane. After another weighing, the test-tube was sealed up, and sampled for analysis. 0.5—0.7 g was burnt. The combustion products were absorbed by a $^1/_{20}$ n solution of Na_2CO_3 which was titrated, in the presence of methyl-orange, with a $^1/_{20}$ n solution of HCl. The results of similar experiments showed a difference of 0.001—0.004%.

This was also the discrepancy between the average data of repeated analyses.

As to testing methods, they were on the whole the same as used in the case of elementary sulphur solutions. After a prolonged contact of the mercaptans with iron in sealed tubes, both the metals and the solutions were tested.

While in those experiments where the metal had not experienced any change a thorough analysis of the solutions was, from the point of view of corrosion, practically superfluous, being only a further corroboration of the lamp method of analysis, it was of the utmost importance in those experiments where the metal had been attacked, since it enabled the experimenters to form a judgment of the factors responsible for the corrosion.

The results of the experiments are shown in the table given on page 414.

Representative Analysis

Experiment 13

A sample of 1.2678 g butyl-mercaptan solution was analysed after having been in contact with iron for 800 days.

As described above, the solution was diluted with hexane to 5.8144 g.

The concentration of «mercaptan» sulphur in the solution before its contact with iron was 0.347%.

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* Owing to cyclohexane's higher boiling point, which greatly facilitates experimenting, the writers have used it as a solvent for the mercaptans, in preference to hexane, which they had employed in their experiments with elementary sulphur.

Consequently, the sample analysed must have contained 0.0044 g sulphur as butyl-mercaptan, unless it had reacted with Fe, its concentration in the diluted solution being 0.076%. Taking into account the sulphur content of the solvents, which is practically the same for both of them (0.011% for cyclohexane and 0.010% for hexane), and assuming in our calculations the concentration of sulphur to be 0.010%, the total percentage of sulphur in the solution burnt is 0.086%.

Burning

In two parallel analyses the following amounts were burnt

I. 0.4768 g. II. 0.4628 g.

Titration

I. 21.10 cm^3—20.65 cm^3=0.45 cm^3~1/20 *n* HCl.

0.45 $cm^3 \times 1.1951 = 0.54$ cm^3 1/20 *n* HCl.

II. 21.10 cm^3—20.68 cm^3=0.42 cm^3~1/20 *n* HCl,

0.42 $cm^3 \times 1.1951 = 0.50$ cm^3 1/20 *n* HCl.

Calculation

$$\text{I.}\ \frac{0.0008 \cdot 0.54 \cdot 100}{0.4768} = 0.090\%$$

$$\text{II.}\ \frac{0.0008 \cdot 0.50 \cdot 100}{0.4626} = 0.086\%$$

Average 0.088%.

Theoretical value, 0.086; analysis, 0.088.

The discrepancy is within the limits of errors involved in the method of analysis.

It may be seen that in the majority of the experiments the specimens of iron have remained unchanged in spite of a very prolonged contact with mercaptan, the only exception being Experiment 14, with butyl-mercaptan, where the iron was coated with a precipitate that outwardly resembled rust. The coating was subjected to a micro-chemical investigation, which convinced us of the total absence of sulphur in it. The method used in analysing the coating was as follows. Its grains were wetted on the object glass with a 5% solution of calcium chloride, the drop being then treated with bromine water vapour. In no case did the subsequent microscopic examination of the drop disclose, the presence of $CaSO_4$, which must have been formed, had the coating contained any sulphur. In the control experiments, however, where the amounts of iron sulphide were still smaller, it has always been possible to observe the characteristic needle-shaped crystals of calcium sulphate.

The results of the analyses would thus suggest that the coating consisted of iron oxides, extraordinary as their formation might seem in the conditions of our experiments.

Another point to be noted is that the analyses of the solutions (including that used in Experiment 14) failed to disclose any deficiency of sulphur therein, which would naturally have been apparent, had the mercaptans reacted with the iron.

All these facts justify the conclusion that, in the conditions studied by the writers, the solutions of ethyl- or butyl-mercaptans in cyclohexane do not affect metallic iron.

Conclusions

1. It has been proved that iron is unaffected by solutions of ethyl- or butyl-mercaptans in cyclohexane.

2. It has been confirmed that, subject to certain conditions, the lamp method is an accurate enough method of analysis of sulphur.

Received
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

BIOCHEMISTRY

NEW SOLVENTS OF GLUTEN PROTEINS

By M. I. KNIAGINIČEV and T. M. GORELKINA

(Communicated by N. I. Vavilov, Member of the Academy, 29. VII. 1937)

A study of wheat proteins for the last 25—30 years has shown that no adequate idea of the baking quality of flour or grain can be formed by characterizing the protein according to their solubility or aminoacid composition. It has been proved, however, that the quantity and quality of protein is a factor of outstanding importance in determining of the baking properties of wheat. The customary notion of gluten as consisting of the two proteins, gliadin and glutenin, is subject to doubt, because by mixing these two proteins a preparation is obtained fundamentally different from the initial gluten. Up to the present time, however, gluten proteins are characterized and identified by their solubility in salt, alcohol and alkali solutions, which permitted Osborne to classify on this principle the plant proteins into a definite system.

Thus, the urgency in looking for new ways of investigation of the gluten proteins, ways which will yield new data on their chemical properties makes itself felt.

One of the promising ways, it would appear, is to find solvents which would, firstly, completely dissolve the gluten proteins and, secondly, on their precipitation from these solvents a protein preparation should be obtained with physical and chemical characteristics closely resembling those of the initial natural gluten.

Theoretically, according to H. K. Meier and H. Mark, it is possible to find solvents which will completely bring into solution plant proteins. Works have appeared in the present day literature recording the complete solubility of gluten proteins in a dilute solution of salicylic sodium. We corroborate the statements of these writers.

Along with this we have found the following neutral and alkali solvents which completely dissolve the wheat gluten proteins.

Neutral solvents:

1) 10% dilute salicylic sodium solution,
2) 10% dilute benzoic sodium solution,
3) 10% salicylic sodium solution in 50% alcohol,
4) 10% benzoic sodium solution in 50% alcohol,
5) glycerine specific weight 1.23.

Alkali solvents:

6) 0.2% caustic sodium solution in 50% ethyl alcohol.

The protein solutions in the above mentioned solvents are very stable, and in the course of several days show no marked spontaneous precipitation.

For a further study of the protein complex of the wheat gluten we have precipitated the proteins from water and alcohol solutions of salicylic sodium and benzoic sodium by crystalline magnesium sulphate (non-crystalline magnesium sulphate effects precipitation but poorly if at all) and from a glycerine solution by repeatedly diluting them with water four times.

The proteins obtained after the precipitation and the dialysis (from neutral solvents), although different from the initial gluten by their physical properties, were characterized, however, by elasticity and other properties of the initial natural gluten. It should be observed hereby that the physical properties of the gluten were increasing considerably on crushing the gluten proteins preparation between the fingers.

Their water capacity (63.15%) was near to that of the natural initial gluten (67.30%). The proteins precipitated from the glycerine solution had physical properties superior to those of the initial gluten.

On diluting the glycerine solution of the gluten by several parts of 96% alcohol no precipitation of the proteins could be noticed in the course of several days. This points certainly to the fact that a reaction between the proteins particles and glycerine takes place, and that this combination of protein and glycerine is well soluble in ethyl alcohol. An alcohol solution of glycerine does not dissolve the gluten completely.

On extracting the gluten complex from an alcohol solution of alkali a protein preparation was obtained deprived of those physical properties by which the natural initial gluten is characterized.

The gluten complex of proteins obtained after precipitation and dialysis by its solubility in salt (5%), alcohol (70%) and alkali (0.2 %) solutions approaches the initial gluten, as may be seen from Table 1.

Table 1

Fractional Distribution of Proteins in the Initial and in the Precipitated Glutens of the Variety *Hordeiforme* 0189, Grown on the Valuisky plot (Volga German Republic)

(Per cent of the total N)

Preparations of gluten proteins and method of precipitation	Total N	Salt soluble N	Alcohol soluble N	Alkali soluble N	Rest N
Natural initial gluten dried in room temperature	100	9.3	19.8	70.8	0.1
Gluten precipitated from 10% dilute benzoic sodium solution	100	3.8	28.1	68,0	0.1
Gluten precipitated from 10% dilute salicylic sodium solution	100	13.7	36.2	50.0	0.1
Gluten precipitated from 10% alcohol solution of benzoic sodium . .	100	4.1	34.2	61.0	0.7
Gluten precipitated from 10% alcohol solution of salicylic sodium .	100	6.6	27.4	64.8	1.2
Gluten precipitated from glycerine solution	100	7.7	23.7	67.8	0.8

The gluten proteins precipitated from a glycerine solution are the least subject to variations in solubility. In the protein preparations, as may be

seen from Table 1, the alcohol soluble fraction increases at the expense of the two remaining ones.

Preparations of gluten proteins obtained from dilute solutions of sodium benzoate, of other varieties and species of wheat grown at different places of the USSR, are characterized by similar modifications in the distribution of different protein fractions. The data from the Dnepropetrovsk plot (Table 2) will serve as an example.

Table 2

Fractional Distribution of Proteins in the Initial and in the Precipitated Glutens of Different Varieties of Wheat Grown on the Dnepropetrovsk plot (Ukraine). 1935

(Per cent of the total N)

Wheats	Gluten preparation	Total N	Salt soluble N	Alcohol soluble N	Alkali soluble N	Rest N
Triticum monococcum L. gr. *flavescens* Körn (sample of the world collection of the Inst. of Plant Industry No. 20631)	Initial	100	4.7	7.5	87.6	0.2
	Precipitated	100	5.8	17.7	76.5	0.4
Triticum durum Desf. *expansum*, gr. *hordeiforme* Host. (var. *hordeiforme* 0189)	Initial	100	12.3	21.5	65.8	0.4
	Precipitated	100	11.6	37.8	50.2	0.4
Triticum vulgare Host., *indo-europeum* Var. gr. *erythrospermum*. Körn (var. Novinka)	Initial	100	4.1	11.8	83.3	0.8
	Precipitated	100	3.3	13.9	82.6	0.2

From the above data it will be seen that the protein complex of wheats belonging to three genetic groups differs in the relative quantity of the fractions of gluten protein.

From this example it will also be seen that in the precipitated gluten the alcohol soluble fractions increases at the expense of other protein fractions. Analysis of wheats grown on the Moscow plot have shown like results.

Thus, the character of properties variations of solubility of the precipitated gluten proteins in salt solutions, alcohol solutions and alkali solutions remains essentially the same for different varieties of wheat. The amount of phosphorus in the initial gluten (0.24%) closely approaches that of the precipitated one (0.20%).

The fractional precipitation of proteins by varying the strength of the magnesium sulphate solution results in preparations identical with the initial, natural gluten.

Some differences between the natural and the precipitated gluten are, apparently, to be accounted for by various disturbations of combination among the protein particles in the process of its dissolution. It is to be supposed that while the aggregates formed in the precipitation of the gluten retain the inverse property of forming again an elastic gluten protein, there occurs some disturbation of the combining property the latter being indispensable if a gluten identical with the natural one is to be obtained.

It is known to day that the gluten of wheat proteins contains in its composition some substances (fats and others) organically combined with the protein. The separation of these substances brings about an abrupt alteration of the physical properties of the gluten. It is possible that this phenomenon takes place in the case under consideration. A further careful study of the gluten proteins will bring to light the true causes of the alteration of properties of the gluten proteins observed during their precipitation.

Conclusions

1. The solubility of proteins in salt, alcohol and alkali solutions cannot serve as a basis for the classification of proteins.

2. Plant proteins may be regarded as one protein complex which can be completely dissolved in neutral as well as in alkali solutions.

3. The new neutral solvents, which entirely dissolve the gluten proteins, make it possible (on precipitating the proteins from them) to obtain preparations identical with the initial natural gluten both as regards their solubility (in salt, alcohol and alkali solutions) and their physical properties.

4. An alcohol solution of alkali, while completely dissolving the gluten proteins, gives on precipitation a protein entirely different by its physical properties from the initial gluten.

5. The gluten proteins of various wheat species, grown at different parts of the USSR, on precipitation from neutral solvents, increase the alcohol soluble fraction of the proteins at the expense of the alkali or salt soluble fraction in comparison with the initial natural gluten.

6. Wheats belonging to different genetic groups differ in solubility of the gluten proteins in solvents.

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Received
29. VII. 1937.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

GENETICS

A FROST-RESISTANT TRIPLE POTATO HYBRID *SOLANUM ACAULE* × *S. TUBEROSUM* (FÜRSTENKRONE) × *S. TUBEROSUM* (CENTIFOLIA)

By L. A. DREMLIUG

(Communicated by N. I. Vavilov, Member of the Academy, 29. VII. 1937)

In connection with the unusually early autumn frosts in the far north occurring ordinarily in July and August, the creation of frost-resistant varieties of potatoes by means of interspecific hybridization between *Solanum tuberosum* L. and wild frost-resistant species is of particular importance for this region. Among the latter species *S. acaule* Bitt. is of the greatest interest.

S. acaule is a wild, mountain species, which grows at altitudes as high as 5 000 m in its native habitat, extending from Peru to Argentina. The specimen used in this investigation was collected by S. V. Juzepczuk at Cerro de Pasco, Peru, and classified as *S. acaule* var. *subexinterruptum* Bitt. It withstands frosts, under field conditions at Khibini, as low as—8°C, without injury to the leaves. The dark green leaves of *S. acaule* form a rosette near the surface of the ground. They are 0.40 mm thick, while the average thickness of potato leaves is 0.18—0.26 mm. The flowers are small, bluish-purple in color, and are borne not on branched peduncles but on short pedicels. Pollen fertility ranges from 80 to 100 per cent. This species produces an abundance of seed-balls in each of which there are more than 100 seeds. Under conditions at Khibini and also in Leningrad and Moscow regions, *S. acaule* yields tubers only under a short day. The tubers are small and white with bluish-purple sprouts.

The first hybrid between *S. acaule* and *S. tuberosum* (variety Fürstenkrone, with white flowers and tubers) was obtained by M. S. Blagovidova in 1932 at the Potato Institute in Moscow. It should be noted that it is in general very difficult to make successful crosses between *S. acaule* and *S. tuberosum*. The *S. acaule* × Fürstenkrone hybrids in the early stages of their development form a rosette of leaves like that of *S. acaule*, but, as development proceeds, there grows up from the rosette a stem pigmented with bluish-purple anthocyanin. This stem reaches a height of 24—30 cm. The flowers are bluish-purple, but they are larger than those of *S. acaule* and are borne on a branched peduncle. Pollen fertility ranges from 20 to 30 per cent. Under conditions of a short day this hybrid yields tubers which are white with a bluish tinge. It withstands frost of —3° C.

In 1934 tubers of the hybrid *S. acaule* × Fürstenkrone were planted at the Polar Station. At the end of August, when the temperature was already

quite low, I. A. Veselovsky crossed these hybrids with *S. tuberosum* (variety Centifolia, with reddish-purple flowers and pink tubers). The seed-balls produced contained very few seeds. In 1935 from these seeds seven plants were grown. Only two of these plants yielded tubers, very small ones (10—12 g), and only under conditions of a short day.

In 1936 from these tubers of the hybrid *S. acaule* × Fürstenkrone × Centifolia we succeded in growing six plants. Cuttings from all these took root. Some of the plants were left in the coldframes and some were planted in the field. Like the parental hybrids *S. acaule* × Fürstenkrone, the triple hybrids first form a rosette of leaves near the ground, and later send up stems from 16 to 23 cm in height. The stems are pigmented with bluish-purple anthocyanin. The leaves are solid, dark green. The flowers range in color

Fig. 1. Triple hybrid *S. acaule* × Fürstenkrone × Centifolia.

from light to dark bluish-purple, and are borne on a short branched peduncle (Fig. 1).

The triple hybrid plants flowered in profusion. Pollen fertility varied widely. Thus, in plant No. 34 it ranged from 35.5 to 56.2 per cent and in plant No 28 from 50 to 85.2 per cent. The hybrids formed seed-balls by both artificial and natural self-pollination. These seed-balls contained from 33 to 50 seeds. In the field under conditions of a long day the hybrids produced very small tubers; in the coldframes under conditions of a short day they yielded 255 g of tubers per plant. The tubers are white with bluish-purple streaks. The eyes are bluish-purple. On September 26 these triple hybrids, growing in the field, withstood a frost of—5.5° C with a relative humidity of 65 and a deficit of humidity of 0.7. Only the flowers were injured.

In order to produce from this exceptionally frost-resistant hybrid—(*S. acaule* × Fürstenkrone) × Centifolia—frost-resistant varieties of potatoes, with good tuber-formation under conditions of a long day, the hybrid was cros-

sed with *S. tuberosum* (commercial varieties Centifolia and Fürstenkrone and Veselovsky's Seedling 423). The seed-balls formed contained 37—63 seeds each.

For the cytological analysis of the hybrid *S. acaule* × Fürstenkrone × Centifolia and also of the hybrid *S. acaule* × Fürstenkrone root-tips and buds were fixed in Navashin's solution. Root-tips were cut into sections 7 microns thick; buds, into sections 10—11 microns thick. The preparations were stained with Heidenhain's iron-haematoxylin. The figures were drawn at a magnification of 3 200.

In cells in the growing zone of root-tips of different plants there were counted 72 and 74 chromosomes (Fig. 2). Since both *S. acaule* and *S. tuberosum* have 48 as their diploid chromosome number, the triple 72-chromosome hybrid (*S. acaule* × Fürstenkrone × Centifolia) apparently originated from the union of a unreduced gamete of the hybrid *S. acaule* + Fürstenkrone, having 48 chromosomes, with a normal gamete of *S. tuberosum* (variety Centifolia), having 24 chromosomes. Plants with 74 chromosomes presumably arose as a result of non-disjunction of one pair of chromosomes in *S. tuberosum* during meiosis.

Fig. 2. Somatic plate; $2n = 74$. *S. acaule* × Fürstenkrone × Centifolia.

Fig. 3. Somatic plate; $2n = 139$. *S. acaule* × Fürstenkrone × Centifolia.

Fig. 4. First metaphase. *S. acaule* × Fürstenkrone × Centifolia.

Fig. 5. First anaphase. *S. acaule* × Fürstenkrone × Centifolia.

Fig. 6. Second metaphase. *S. acaule* × Fürstenkrone.

As we have already mentioned, the triple hybrid was obtained from crosses made during low temperature in the fall. It may be that this low temperature promotes the formation of unreduced gametes. In one of the hybrid plants in the growing zone of root tips there were found not only cells with 74 chromosomes but also cells with 139—142 chromosomes (Fig. 3), i. e., having almost a double number of chromosomes. At meiosis, at first metaphase, there were counted from 34 to 42 bodies. In Fig. 4 is shown a metaphase plate with 36 bodies. Some of them are quite small, presumably univalent chromosomes of *S. acaule*. There are four large bodies, consisting of two elements lying close together. Whether or not these bodies and some

of the other large bodies in the plate are multivalents or secondary associations of bivalents it is difficult to say, since we did not investigate diakinesis ([1],[2]).

At first anaphase there are observed lagging univalents in the process of dividing. The two halves usually pass together to the same pole. In Fig. 5 (first anaphase) we see a considerable number of lagging chromosomes in the process of dividing. At second metaphase both of the triple hybrid and of the parental hybrid, *S. acaule* × Fürstenkrone, there is again observed what appears to be secondary association of chromosomes (Fig. 6). At second metaphase there are sometimes observed cells with only one plate. At second anaphase lagging chromosomes are not seen. Tetrad formation is regular.

Conclusions

1. The hybrid *S. acaule* × Fürstenkrone constituted an intermediate step in obtaining frost-resistant varieties of potatoes. Its low pollen fertility (20—30%) under normal temperature conditions, making it impossible to obtain seed-balls, constituted a great obstacle to further work. Under conditions of lowered temperature the formation of unreduced gametes by the hybrid *S. acaule* × Fürstenkrone made it possible in crosses with *tuberosum* to obtain seed-balls, thereby enabling us to advance the work to the next stage.

2. The formation of unreduced gametes in the hybrids under conditions of low temperature and also the presence in the somatic tissue of the triple hybrid of almost a double number of chromosomes ($2n = 72$; in somatic tissues 139—142 chromosomes) makes it possible to undertake the production of amphidiploid potatoes by self-pollination of hybrids under conditions of low temperature and by the action of different agencies on the vegetative organs of the plants. If fertile, constant progeny are obtained, this will solve an important problem for the far north—seed material giving non-segregating progeny.

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Received
29. VII. 1937.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

GENETICS

NEW FIXATIVES FOR CHROMOSOME MORPHOLOGY

By M. V. FAVORSKIJ

(Communicated by N. I. Vavilov, Member of the Academy, 19.VI.1937)

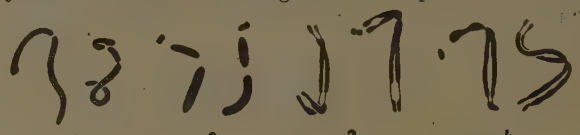
The object of this investigation was to test new fixatives suitable for the study of chromosome morphology, and to improve their properties as such. All the experiments were made on root tips of seedlings of barley (*Hordeum vulgare* L. var. *pallidum*), permanent preparations stained with haematoxylin being used in all instances. Fixation lasted 24 hours in all cases.

G. A. Lewitskij ([2],[3]) has shown that mixtures of formalin with salts of a number of heavy metals produce an action favourable to the study of the articulation of chromosomes. The tests made by the writer with mixtures of formalin and lead nitrate, formalin and ferric chloride, and formalin and uranyl nitrate, suggest the same conclusion. Of practical interest are mixtures of formalin and uranyl nitrate. Thus, a mixture of 5 parts of a 2% water solution of a freshly recrystallized uranyl nitrate, $UO_2(NO_3)_2\,6H_2O$, often used in photography, with 5 parts of a 10% formalin (obtained from commercial 40% formaldehyde), is a fixative capable of bringing out kinetic and some akinetic constrictions. Chondriosomes are preserved in about the same manner as in using G. A. Lewitskij's([1]) weak chrome-formalin. This mixture may be termed «weak uranyl-formalin». A mixture of equal volumes of 5% $UO_2(NO_3)_2\,6H_2O$ and 50% formalin («strong uranyl-formalin») brings out the kinetic constrictions and appendages in the first pair of chromosomes, the constrictions being rather wide achromatine breaks. The chondriosomes easily become discoloured, but the chromosomes also lose colour fairly rapidly. The plasm remains rather dark. Thus, neither mixture ensures an adequate articulation of chromosomes, giving either a dark plasm, or well preserved chondriosomes. They differ in this respect from Lewitskij's([2]) platino-formalin fixatives, which are now coming into increasing use and make it possible to obtain dark, well-articulated chromosomes, standing out sharply against a background of a «clear» translucent plasm, with no trace of its stained formal elements, the chondriosomes. It is known that a «clear» plasm may be obtained by using acid fixatives, as, for instance, Navashin's or Bouin's mixtures, etc. These mixtures, however, have not proved quite suitable for studying the chromosome morphology of most plants([1]). Our object was to obtain a mixture with an acid content that would give well-articulated chromosomes on a background of a sufficiently clear plasm. Our experiments were mainly intended to improve the properties of strong uranyl formalin as a fixative, that substance being known to yield breaks particularly well defined and presumably allowing of considerable additions of acid without impairing the articulation of the chromosomes. In addition to this, strong uranyl-formalin, as well as strong chrome-formalin([2]), is not in itself a fixative of chondriosomes. Sulphuric acid and trinitrophenol were added. The latter gives a very pale plasm if mixed with formalin and is recommended

by G. A. Lewitsky(2) as «picro-formalin», an independent fixative suitable for use in studying chromosome morphology. As a result of tentative additions of sulphuric acid we succeeded in making up a mixture that makes it possible to obtain both a fairly clear plasm and well articulated chromosomes. The formula of our mixture is as follows: 5% uranyl nitrate, 10 parts; 100% formalin, 5 parts; 0.1% sulphuric acid (by volume), 5 parts. Name: «uranyl-sulphate-formalin».

The material fixed with this mixture gives, in the case of a strong differentiation of the preparations, very thin, split-up and articulated chromosomes. The chromosomes are finer than those obtained with platino-formalins or chrome-formalins, and have primary and secondary constrictions resembling the finest of filaments. If differentiation is not carried so far, the chromosomes are not so fine, but non-discoloured chondriosomes are preserved in the cells of the peripheral portion of the root. By experimenting with additions of trinitrophenol, the following mixture was evolved: 5% uranyl nitrate, 10 parts; 100% formalin, 5 parts; trinitrophenol (sat. aq. sol.), 5 parts. Suggested name: «uranyl-picro-formalin».

Upon fixation with uranyl-picro-formalin, fine, well-articulated chromosomes may be obtained on a background of a plasm of much lighter hue



Individual chromosomes from nuclear plates of barley, fixed by *1*—a weak uranyl-formalin solution; *2*—a strong uranyl-formalin solution; *3*—uranyl-sulphate-formalin; *4*—uranyl-picro-formalin.

than this is possible upon fixation with strong uranyl-formalin. In the cells of the peripheral portion of the root, stained chondriosomes are partially preserved. No complete destruction of the chondriosomes could have been expected in this case, as the latter are still partially preserved even upon fixation with A. G. Lewitskij's picro-formalin. It is a remarkable fact that an addition of trinitrophenol to strong uranyl-formalin, far from interfering with the articulation of the chromosomes, renders the latter finer and more distinctly articulated. This is illustrated by the figure showing individual chromosomes from nuclear plates, fixed by the mixtures described in this paper. On the whole, by using either uranyl-sulphate-formalin or uranyl-picro-formalin in our fixation experiments, we were able to observe all the types of articulation of chromosomes as described by G. A. Lewitskij(1) for *Hordeum vulgare* L., var. *pallidum*. Both these mixtures, therefore, although possibly inferior to platino-formalin fixatives in giving perhaps chromosomes of too great a fineness and not fully discoloured chondriosomes, may, nevertheless, be classed amongst suitable fixatives for chromosome morphology, one of their advantages being their cheapness and accessibility. It is probable that, by adding small amounts of highly dilute acids to weak chrome-formalin or to other chondriosome fixatives, which bring out the morphology of chromosomes, one would succeed in evolving mixtures similar in action to those obtained by us, or even superior to the latter in point of quality.

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Received
19. VI. 1937.

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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

ANIMAL PHYSIOLOGY

CONCERNING THE COCHLEAR POTENTIALS IN MAN

By G. V. GERSHUNI, A. M. ANDREEV and A. A. ARAPOVA

(Communicated by L. A. Orbeli, Member of the Academy, 23. VI. 1937)

In 1930 Wever and Bray(7) described the rise of alternating electrical potentials, which could been observed during sound stimulation, when electrodes leading to an amplifier were applied to the cochlea or the auditory nerve of an animal.

This interesting phenomenon was further studied in detail by a number of investigators (1,2) and was used as a very important method of analysis of physiological processes occurring in the cochlea and the auditory nerve.

It must be stated, however, that up to the present the cochlear potentials were thoroughly studied only in animals, whereas several problems of auricular physiology and, in the first place, the problem of interrelation between the magnitude of cochlear potentials and the intensity of the auditory sensations [see Stevens and Davis(5)] could have been solved with sufficient clearness only by experiments performed on humans.

Fromm, Nylén and Zotterman(4), Undritz(6) attempted to study the cochlear potentials on man. But the scope of potentials they obtained after amplification were to small to permit any measurement and oscillographic record.

In this paper we communicate some data of our study of the cochlear potentials in man.

Methods

The experiments were performed on persons having total lesion of the ear drum. The electrode, consisting of a thin silver wire (diam. 0.2 mm) in a rubber tube, was fixed on the promontory in the same way as described by Fromm et al. (4). A silver plate fastened to the back of the forearm served as an inactive (grounded) electrode.

Two joined ebonite tubes, one for the electrode, the other for the conducting of sound were introduced into the external auditory meatus.

The sound was conveyed to the ear either from an ordinary whistle or from a rubber hose (diam. 3 cm) which was connected with a moving coil loudspeaker. An oscillator and a 10-w. amplifier were electrically connected with the loudspeaker. The sound pressure was measured by a condenser microphon in the same manner as described by Davis, Derbyshire, Lurie a. Saul (3).

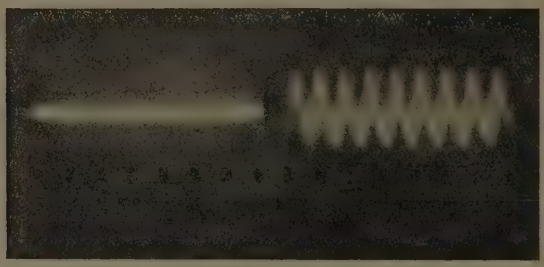
The electrodes were connected with the input of a 4-valve resistance-capacity coupled amplifier. The amplified tension was led to a cathode ray oscil-

lograph with internal synchronization. The recurrent waves obtained on the screen of the cathode-ray oscillograph were photographed. The total amplification of the system was about 800.000 times.

Results

Experiments on 5 subjects were performed. It must be stated that in the majority of cases the amplitude of the potentials after amplification was so small, that it was difficult to obtain oscillographic records and the potentials could only be revealed by a ear-phone as described by Fromm et al. But after many trials, the amplitude of the cochlear potentials obtained in one of the subjects reached a value which was quite sufficient for oscillographic recording. In this case, the sound pressure being near 250 bars, the input potentials were found to be about 8 microvolts.

The figure represents an oscillogramm of the cochlear potentials in man. The straight line on the oscillogramm is obtained by interrupting the sound



conduction to the ear by pressing the rubber tube. The disappearance of the alternating potentials in this case proves that the effect does not depend on any distorting influence on the amplifying system.

Oscillographic records of the cochlear potentials could be repeatedly obtained in the course of an experiment, but a slight displacement of the electrode in the middle ear was sufficient to cause the phenomenon to vanish.

The loss of hearing by the subject under experiment did not exceed 30 db at the range of frequencies from 500 up to 5 000 cycles p. s.

At 2 000 cycles (the frequency of the oscillographic record) the hearing loss was 10 db.

The data obtained show that cochlear potentials in man can be studied quantitatively, but their detection, depending to a large degree on the position of the electrode in the middle ear, is bound with a number of technical difficulties which render the study of this phenomenon in man much more complicated than in animals.

We hope communicate more detailed data of a quantitative study of cochlear potentials in the near future.

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Received.
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Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 8

PLANT PHYSIOLOGY

ON THE SALT RESISTANCE OF THE COTTON PLANT. LOCALIZATION OF SALTS IN THE LEAVE TISSUES

By V. S. SHARDAKOV

(Communicated by A. A. Richter, Member of the Academy, 13. VII. 1937)

Some halophytes possess anatomical devices for the elimination of salts. Such are, for instance, the salt glands of the species: *Statice*, *Tamarix*, *Reaumuria*; the stomata of the *Aelunopus littoralis*, and others. The presence of these organs and their function has been established by many authors: Volkens (1), Marloth (2), Schscherback (3), Ruhland (4), Keller (5); see also Shardakov (6).

The salt-eliminating glands, however, are not the only organs enabling the plant to remove the excess of salts from some of the tissues. Thus, for instance, in plants of the family *Chenopodeae*, the under surface of the leaves is covered with a dense gray film formed of spheroid hairs. Analyses of these hairs (Mehlhaare), made by Lukaszewiz (7), show that their cell sap has a very high content of potassium chloride. As the leaf grows, these hairs gradually fall off, thus liberating the plant of its salts. But even prior to the fall of these hairs the salts contained in them are outside of the sphere where the main physiological processes of the leaf take place.

Such a localization of salts in the tissues whose functions are not affected by an excess of salts, e. g. in epithelial tissues, is to a certain extent tantamount to their elimination.

The localization of salts in the leaves must be of exceptionally great significance, for, on the one hand, it is there that the greatest quantity of mineral elements is accumulated and, on the other,—it is there that the most important physiological process—photosynthesis—takes place. In plants with lamellar leaves, the relative mass of epithelial tissues (the epidermis and its derivatives) is greater in the leaves then in other organs of the plant.

On the basis of what had been set forth concerning the cotton plant's salt resistance, which is very high*, it was necessary to study the distribution of salts in the different leaf tissues. The cotton plant possesses neither salt-eliminating glands nor falling hairs of the type observed in *Chenopodae*; it was, however, to be expected that salts are localized in some of the tissues.

The importance of elucidating this problem was enhanced by the fact that the cotton plant, when growing on saline soils, accumulates consider-

* Balls (8) refers the cotton plant to facultative halophytes: «Egyptian cotton (*Gossypium peruvianum*) may be classified as a facultative halophyte».

able quantities of salts. This has been established by a number of authors: Rogalski (9), Harris (10), Novikov (11), Shardakov (1930), etc.

For the purpose of ascertaining the localization of salts, the presence of Cl and K was determined by the microchemical qualitative reactions of Molisch (12). The plants were taken from the plot of the Physiological Laboratory of the Central Plant Breeding Station of the Cotton Institute, and from the saline plots of the former Ferghana Experiment Station (Fedchenko railway station). The leaves of *Gossypium hirsutum*, Navrotski variety, were taken for investigation during the flowering stage.

Analyses have shown that Cl and K accumulate in the leaves of the cotton plants, namely in the epidermis, glandular hairs, lining-cells of the internal (oil-secreting) glands and leaf nectaries. On soils having a high salt content, chlorine occurs likewise in the cells of the assimilating parenchyma and in the guard cells of the stomata, but in smaller amounts than in the previously mentioned sites of localization. It is to be supposed that the accumulation of salts in the chlorophyl-bearing parenchyma occurs only when the cells of epidermal and glandular hairs are full.

At the same time the presence of chlorine in the chlorophyl-bearing parenchyma of the cotton plant grown on saline soils prevents us from explaining the salt resistance of the cotton plant by the phenomenon of localization only.

It would be interesting to study the localization of salts in the cotton plant as well as in other plants in greater detail extending the investigation to other organs, different phases of growth and different species and varieties.

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Received
13. VII. 1937.

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